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(19)

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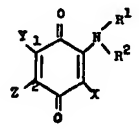
(54) HERBICIDAL COMPOSITIONS CONTAINING 1,4-QUINONES OR DERIVATIVES THEREOF

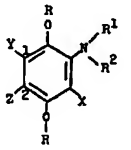
(71) We, SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V., a company organised under the laws of The Netherlands, of 30 Carel van Bylandtlaan, The Hague, The Netherlands, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:–

This invention relates to herbicidal compositions containing as active ingredient a 1,4-quinone or derivative thereof and to a method of controlling undesirable plant growth.

The present invention provides a herbicidal composition comprising a carrier together with as active ingredient a compound having one of the following general formulae:–



(I)



(II)

wherein

R^1 is hydrogen, alkyl, alkoxy, alkylcarbonyl, cycloalkyl, or an -NO or $-CONR^3R^4$ group;

R^2 is hydrogen, alkyl, alkoxy, alkylcarbonyl, cycloalkyl, aryl or an -NO or $-CONR^3R^4$ group;

X is halogen, alkoxy, or an $-NR^3R^4$ or -NHCOO alkyl group;

R^3 and R^4 each individually represent hydrogen, alkyl, aminoalkyl or alkylaminoalkyl;

Y and Z together with carbon atoms 1 and 2 represent a benzene, thiophen, thiadiazole or thiazole ring each of which rings may be substituted by an alkyl group; and

R is alkyl, alkylcarbonyl or arylcarbonyl, the alkyl or aryl groups of which may be optionally substituted by halogen;

or where the compound is capable of forming a quaternary ammonium salt, the quaternary ammonium salt thereof; provided that

(a) for the groups alkoxy, alkylcarbonyl, NO and -CONR^{3}R^4, R^1 is not the same as R^2;
(b) in formula (I) R^1 or R^2 can only be an alkylcarbonyl group when Y and Z together with carbon ato s 1 and 2 form a thiopen, thiazole or thiadiazole ring;
(c) when R^1 is hydrogen and R^2 is alkylcarbonyl X does not represent an -NH alkyl group; and
(d) when R^1 is hydrogen and R^2 is alkyl, X does not represent an -NHCOO alkyl group.

The preferred composition according to the invention has as active ingredient a compound of formula (I) or (II) above wherein, together with the provisos (a) to (d):–

R^1 is hydrogen, alkyl of 1 to 4 carbon atoms (e.g. methyl, ethyl, isopropyl), cycloalkyl of up to 6 carbon atoms (e.g. cyclopropyl), alkoxy of 1 to 4 carbon atoms, alkylcarbonyl of 2 to 5 carbon ato s, or an -NO or CONR^{3}R^4 group;

R^2 is hydrogen, alkyl of 1 to 4 carbon atoms (e.g. methyl, ethyl, propyl, isopropyl), alkoxy of 1 to 4 carbon atoms, alkylcarbonyl of 2 to 5 carbon atoms (e.g. methylcarbonyl, ethylcarbonyl), or a -CONR^{3}R^4 groiup (e.g. aminocarbonyl, methylaminocarbonyl, dimethylaminocarbonyl, diethylaminocarbonyl, isopropylaminocarbonyl);

X is chlorine, bromine, alkoxy of 1 to 4 carbon atoms (e.g. methoxy, ethoxy, isopropoxy), NR^{3}R^4 (e.g. amino, methylamino, dimethylamino, isopropylamino, dimethylaminoethylamino, dimethylaminopropylamino), or an -NGCOO alkyl group of up to 5 carbon atoms (e.g. methoxycarbonylamino);

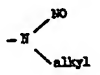
R^3 and R^4 each individually represent hydrogen, alkyl of 1 to 4 carbon atoms (e.g. methyl, isopropyl), aminoalkyl of 1 to 4 carbon atoms (e.g. aminoethyl), alkylaminoalkyl of up to 8 carbon atoms (e.g. dimethylaminoethyl, dimethylaminopropyl);

Y and Z together with carbon atoms 1 and 2 represent a benzene, an alkylbenzene, or a thiophen ring;

R is alkyl of 1 to 4 carbon atoms, alkylcarbonyl of 2 to 5 carbon atoms (e.g. acetyl), arylcarbonyl of up to 15 carbon atoms or haloalkyl of 1 to 4 carbon atoms (e.g. chloroacetyl);

and where the compound is capable of forming a quaternary ammonium salt, the quaternary ammonium salt thereof with an alkyl halide of 1 to 4 carbon atoms (e.g. methyl iodide, chloride or bromide) or with an alkyl sulphate (e.g. dimethyl sulphate).

The compounds of formula I and II can be prepared by conventional synthetic routes and details of these routes can be found in the Examples appearing later on in the specification. However it has been found that one sub-class of the quinones, namely the alkoxy-quinones (i.e. compounds of formula I and II wherein X is alkoxy, preferably having up to 6 carbon atoms), can be prepared by a novel route, which comprises reacting under anhydrous conditions a compound of general formula I or II wherein X is a group of formula:–



wherein the alkyl group contains 1 to 3 carbon atoms, with a monohydric alcohol in the presence of mineral acid, for example hydrochloric acid.

The herbicidal composition according to the invention preferably contains at least two carriers, at least one of which is a surface active agent. A carrier is a material, which may be inorganic or organic and of synthetic or natural origin, with which the active compound is mixed or formulated to facilitate its application to the plant, seed, soil or other object to be treated, or its storage, transport or handling. The carrier may be a solid or a liquid. Any of the materials usually applied in formulating pesticides may be used as carrier.

Suitable solid carriers include natural and synthetic clays and silicates for example natural silicas such as diatomacious earths; magnesium silicates, for example, talcs; magnesium aluminium silicates, for example, attapulgites and vermiculites; aluminium silicates, for example, attapulgites and vermiculities; aluminium silicates, for example, kaolinites, montmorillinites and micas; calcium carbonates; calcium sulphate; synthetic hydrated silicon oxides and synthetic calcium or aluminium silicates; elements such as for example, carbon and sulphur; natural and synthetic resins such as for example, coumarone resins, polyvinyl chloride and styrene polymers and copolymers; solid polychlorophenols; bitumen; waxes such as for example beeswax, paraffin wax, and chlorinated mineral waxes; and solid fertilisers, for example super-phosphates.

Examples of suitable liquid carriers are water; alcohols, for example isopropanol; glycols; ketones, for example acetone, methyl ethyl ketone, methyl isobutyl ketone and cyclohexanone; ethers; aromatic hydrocarbons, for example benzene, toluene and xylene; petroleum

fractions, for example kerosine, light mineral oils; chlorinated hydrocarbons, for example carbon tetrachloride, perchloroethylene and trichloroethane. Compounds which are normally gaseus but which have been compressed to form a liquid may be used. Mixtures of different liquids are often suitable.

A surface active agent may be an emulsifying agent, a dispersing agent or a wetting agent; it may be nonionic or ionic. Any of the surface-active agents usually applied in formulating herbicides or insecticides may be used. Examples of suitable surface-active agents are the sodium or calcium salts of polyacrylic acids and lignin sulphonic acids; the condensation products of fatty acids and lignin sulphonic acids; the condensation products of fatty acids of aliphatic amines or amides containing at least 12 carbon atoms in the molecule with ethylene oxide and/or propylene oxide; fatty acid esters of glycerol, sorbitan, sucrose or pentaerythritol; condensates of these with ethylene oxide and/or propylene oxides; condensation products of fatty alcohols or alkyl phenols for example *p*-octylphenol or *p*-octylcresol, with ethylene oxide and/or propylene oxide; sulphates or sulphonates of these condensation products; alkali or alkaline earth metal salts, preferably sodium salts, or sulphuric or sulphonic acid esters containing at least 10 carbon atoms in the molecule, for example, sodium lauryl sulphate, sodium secondary alkyl sulphates, sodium salts of sulphonated castor oil, and sodium alkylaryl sulphonates such as sodium dodecylbenzene sulphonate; and polymers of ethylene oxide and copolymers of ethylene oxide.

The compositions of the invention may be formulated as wettable powders, dusts, granules, solutions, emulsifiable concentrates, emulsions, suspension concentrates and aerosols. Wettable powders are usually compounded to contain 25, 50 or 75% w of toxicant and usually contain, in addition to solid inert carrier, 3-10% w of a dispersing agent and, where necessary, 1-10% w of stabiliser(s) and/or other additives such as penetrants or stickers. Dusts are usually formulated as a dust concentrate having a similar composition to that of a wettable powder but without a dispersant, and are diluted in the field with further solid carrier to give a composition usually containing ½-10% w of toxicant. Granules are usually prepared to have a size between 10 and 100 BS mesh, and may be manufactured by agglomeration or impregnation techniques. Generally, granules will contain ½-25% w toxicant and 0-10% w of additives such as stabilisers, slow release modifiers and binding agents.

Emulsifiable concentrates usually contain, in addition to the solvent and, when necessary, co-solvent, 10-50% w/v toxicant, 2-20% w/v emulsifiers and 0-20% w/v of appropriate additives such as stabilisers, penetrants and corrosion inhibitors. Suspension concentrates are compounded so as to obtain a stable, non-sedimenting, flowable product and usually contain 10-75% w toxicant, 0.5-15% w of dispersing agents, 0.1-10%w of suspending agents such as protective colloids and thixotropic agents, 0-10% w of a appropriate additives such as defoamers, corrosion inhibitors, stabilisers, penetrants and stickers, and water or an organic liquid in which the toxicant is substantially insoluble; certain organic solids or inorganic salts may be dissolved in the carrier to assist in preventing sedimentation or as antifreeze agents for water.

The compositions of the invention may contain other ingredients, for example, protective colloids such as gelatin, glue, casein, gums, cellulose ethers, and polyvinyl alcohol; thixotropic agents e.g. bentonites, sodium polyphosphates; stabilisers such as ethylene diamine tetra-acetic acid, urea triphenyl phosphate; other pesticides; and stickers, for example non-volatile oils.

Aqueous dispersion and emulsions, for example, compositions obtained by diluting a wettable powder or an amulsifiable concentrate according to the invention with water, also lie within the scope of the present invention. The said emulsions may be of the water-in-oil or of the oil-in-water type, and may have a thick "mayonnaise"-like consistency.

The compounds of the general formulae I and II exhibit a low phytotoxicity towards certain useful crops, especially sugar beet and rice, while at the same time possessing higher phytotoxicity towards many other agriculturally undesirable forms of plant growth. The invention also provides a method of combating undesired plant growth at a locus which comprises applying to the locus a compound of the general formula I or II or a quaternary ammonium salt thereof or a composition according to the invention.

Selective weed control by the process according to the invention may be obtained when the compounds are applied to sown soil before the emergence of plant growth and/or when they are applied to the soil or plant growth after the emergence of crops and/or weeds.

Herbicidal compositions related to those of the present invention are claimed in Specification No. 1 321 101.

The following Examples illustrate the invention.

Example 1 *Preparation of 1,4-diacetoxy-2- acetamido-3- isopropyl aminonaphthalene*

2-Acetamido-3-isopropylamino-1,4-naphthoquinone (3g) was added portion-wise to a

stirred aqueous solution of sodium hydrosulphite ($Na_2S_2O_4$), 50 ml of 10%). After addition and discharge of the red colouration the buff precipitate was filtered off, washed with dilute aqueous sodium hydrosulphite, dried under nitrogen and added to excess acetic anhydride containing a few drops of concentrated H_2SO_4. The mixture was poured into water and the white solid filtered off to give on crystallisation (ethanol) 1,4-diacetoxy-2- acetamido-3-isopropylaminonaphthalene (0.8g).

Analysis	Calculated for $C_{19}H_{22}O_5N_2$	C 63.7; H 6.9; N 7.8%
	Found	C 63.9; H 6.3; N 7.9%

Example 2

By a method analogous to that described in Example 1, 1,4-diacetoxy-2-propionamido -3-chloronaphthalene was prepared, melting point 225°C.

Example 3 - Preparation of 2-(N-methyl-nitrosoamino) -3-(2- dimethylaminoethylamino)-1,4-naphthoquione

2-Dimethylaminoethylamine (2.5 g) was added dropwise to a stirred solution of 2-(N-nitrosomethylamino) -3- chloro- 1,4-napthoquinone (3 g) in ethanol. The mixture was warmed for 1 hour. After cooling, the orange brown solid was filtered off and crystallised (ethanol) to give 2-(N-methyl-nitrosoamino) -3- (2-dimethylaminoethylamino) 1,4-naphthoquinone (2.5 g), m.p. 110°C.

Analysis	Calculated for $C_{15}H_{18}N_4O_3$	C 59.6; H 6.0; N 18.5%
	Found	C 59.4; H 5.9; N 18.4%

Example 4 -Preparation of the methyl iodide salt of 2-(2-N,N-dimethylaminoethylamino) 3-(N-nitroso -N-methylamino) -1,4-naphthoquinone

A solution of 2-(2-N,N-dimethylaminoethylamino) -3-(N-nitroso-N-methylamino) 1,4-naphthoquinone in CH_3CN containing excess CH_3I was allowed to stand for several hours. The precipitate formed was filtered off and crystallised from CH_3CN to give the methyl iodide salt of the starting material. M.pt. 150°C with decomposition.

Example 5 - Preparation of 5-methylamino-6-chloro- 1,2,3-benzothiadiaxole- 4,7-dione

5,6-Dichloro-1,2,3-benxothiadiazole- 4,7-dione (4.7g) in methylene chloride (150 ml) was treated with a 33% solution of methylamine in ethanol (3 ml). After 30 minutes, water (50 ml) was added, the organic phase separated, washed with a further 50 ml of water, drived over $MgSO_4$ and the methylene chloride removed under vacuum. Yield 2.5, m.p. 174.5°C.

Analysis	Calculated for $C_7H_4N_3SO_2C1$	C 36.6; H 1.8; C1 15.5%
	Found	C 36.7; H 2.0; C1 15.7%

Example 6 - Preparation of 5-isopropylamino-6- chloro-1,2,3- benxothiadiaxole- 4,7-dione

This compound was prepared by a method analogous to that of Example 5. It had an m.p. 107-109°C and was prepared in 53% yield.

Analysis	Calculated for $C_9H_8N_3SO_2C1$	C 41.9; H 3.1; N 16.3%
	Found	C 41.2; H 3.2; N 14.2%

Example 7 - 5-(N-methylacetamido) -6-dimethylamino- 1,2,3-benzothiadiazole- 4,7-dione

5-Methylamino-6-chloro- 1,2,3-benzothiadiazole-4,7-dione (1.5g) was dissolved in acetic anhydride (20 ml) concentrated H_2SO_4 was added (20 drops) to the stirred solution. After 30 minutes, (solution turned yellow), this mixture was poured into water (250 ml) and the product extracted with methylene chloride. This 5-(N-methylacetamido)-6- chloro- 1,2,3-benxothiadiazole- 4,7-dione was used without further purification.

The above methylene chloride solution was treated with anhydrous dimethylamine (3 ml) in CH_2C1_2 (20 ml) at room temperature with stirring. After 15 minutes water (50 ml) was added, the CH_2C1_2 solution dried and evaporated. The residue was purified using a silica gel column with 10% Et_2O/CH_2C1_2 as eluant. Yield 0.7g, m.p. 63°C.

Analysis	Calculated for $C_{11}H_{12}N_4SO_3$	C 47.1; H 4.3; N 20.0%
	Found	C 46.7; H 4.4; N 18.1%

Example 8 - 2-Methyl-5-methylamino-6-chloro-benzothiazole-4,7-dione

2-Methyl-5,6-dichloro-benzothiazole-4,7-dione (2.5g) in methylene chloride (150 ml) was treated with a 33% solution of methylamine in ethanol (3 ml) at room temperature. After 15

minutes, the solution was washed with water (2 x 50 ml), the methylene chloride dried, and removed under vacuum. The residue was purified using a silica gel column with 10% ether - CH_2Cl_2 as eluant. Yield 1.36g, m.p. 179-180°C.

Analysis Calculated for $C_9H_7N_2SO_2Cl$ C 44.5; H 2.9; N 11.6; S 13; Cl 14.6
Found C 44.4; H 3.0; N 11.2; S 13; Cl 15.1

Example 9 - Preparation of 2-methyl-5- isopropylamino -6- chloro-benxo- 1,3-thiaxole-4,7-dione

This compound was prepared by a method analogous to that described in Example 8. Yield 54%, m.p. 98°C.

Analysis Calculated for $C_{11}H_{11}N_2SO_2Cl$ C 49.9; H 5.1; N 10.35; Cl 13
Found C 49.5; H 4.2; N 10.2; Cl 13

Example 10 - 2-Methyl-5-(N-methylacetamido) -6- isopropylamino- benzothiaxole- 4,7-dione

2-Methyl-5-methylamino-6-chloro- benzothiazole- 4,7-dione (1.5g) in acetic anhydride (20 ml) was treated with concentrated H_2SO_4 (10 drops) at room temperature with stirring. After the solution had turned yellow (*n*30 mm) it was poured into water (250 ml) and the 2-methyl-5- (N-methylacetamido) -6-chloro- benzothiazole- 4,7-dione formed extracted with methylene chloride.

To this solution was added isopropylamine (3 ml) and the mixture stirred for 30 minutes. Water (2 x 50 ml) was added, and after drying the organic phase, the CH_2Cl_2 was removed under vacuum. The residue was purified using a silica gel column with CH_2Cl_2 as eluant. Yield 0.8g, m.p. 112-115°C.

Analysis Calculated for $C_{14}H_{17}N_3SO_3$ C 54.7; H 5.5; N 13.7; S 10.4
Found C 54.8; H 6.0; N 12.0; S 10.3

Example 11 - Preparation of 5-(N-isopropylacetamido) -6-isopropylamino 2-methylbenzothiazole- 4,7-dione

This compound was prepared by a method analogous to that described in Example 11. Yield 34%, m.p. 176-177°C.

Analysis Calculated for $C_{16}H_{21}N_3SO_3$ C 57.3; H 6.3; N 12.5
Found C 56.4; H 6.4; N 12.1

Example 12 - 6-chloro-5-methylamino-benzothiophen-4,7-dione

5,6-dichloro-benzothiophen- 4,7-dione (4.7g) in methylene chloride (100 ml) was treated with an excess of methylamime, and stirred at room temperature for 30 minutes. After washing with water (2 x 50 ml) the CH_2Cl_2 was dried and evaporated. The residue was purified using a silica gel column with CH_2Cl_2 as eluant. Yield 2.8g, m.p. 192-193°C.

Analysis Calculated for $C_9H_6NSO_2Cl$ C 47.5; H 2.6; N 6.1; Cl 15.6
Found C 47.4; H 2.7; N 6.1, Cl 16.0

Example 13 - Preparation of 6-chloro-5- isopropylaminobenzothiophen -4,7-dione

This compound was prepared by a method analogous to that disclosed in Example 12. Yield 58%, m.p. 110°C.

Analysis Calculated for $C_{11}H_{10}NSO_2Cl$ C 51.6; H 3.9; N 5.5; Cl 13.8
Found C 51.9; H 3.9; N 5.4; Cl 14.1

Example 14 - Preparation of 6-chloro-5-(N-methylacetamido)- benzothiophen-4,7 dione

6-Chloro-5-methylaminobenzothiophen -4,7-dione (2g) in acetic anhydride (20 ml) was treated with concentrated H_2SO_4 (2 drops). After 15 minutes (yellow solution) the solution was poured into water. The yellow acetamido compound was filtered off. Yield 1.25g, m.p. 162-4°C.

Analysis Calculated for $C_{11}H_8NSO_3Cl$ C 46.8; H 3.1; N 5.4; S 12
Found C 48.7; H 3.1; N 5.1, S 11.7

Example 15 - 6-Isopropylamino-5- (N-methylacetamido) benzothiophen-4,7-dione

5(N-methylacetamido) -6-chlorobenzothiophen-4,7-dione (1g) in CH_2Cl_2 (100 ml) was treated with isopropylamine (excess, 3 ml). After 30 minutes the solution was washed with

water (2 x 30 ml), the organic phase dried over $MgSO_4$ and the CH_2Cl_2 evaporated under vacuum. The residual solid was recrystallised from benzene/60-80 P.E. Yield 0.7g, m.p. 172°C.

Analysis Calculated for $C_{14}H_{16}N_2SO_3$ C 57.5; H 5.5; N 9.6; S 10.9
Found C 56.4; H 5.5; N 9.4; S 10.6

Example 16 - *Preparation of 6-isopropylamino-5-(N-isopropyl acetamido) benzothiophen-4,7-dione*

This compound was prepared by a method analogous to that of Example 15. Yield 60%, m.p. 153-154°C.

Analysis Calculated for $C_{16}H_{20}N_2SO_3$ C 60.4; H 5.7; N 8.8
Found C 60.2; H 6.5; N 8.8

Example 17 - *Preparation of 2-dimethylamino-3-(3¹,3¹-dimethylureido) 1,4-naphthoquinone*

2-(Methoxycarboxamido)-3- dimethylamino-1, 4-naphthoquinone (5g) was heted in a sealed tube with an excess of dimethylamine (4g) ethanol (50 ml) at 90°-100°C for 16 hours. After cooling and evaporation of the ethanol the residue was chromatographed on silica gel in CH_2Cl_2. The purple coloured fractions were evaporated to give a solid which on further chromatography gave a red fraction, of the desired compound (0.5g), m.p. 123-124°C.

Analysis Calculated for $N_2O_3C_{15}H_{17}$ C 62.7; H 5.96; N 14.6
Found C 62.5; H 5.9; N 14.7

Example 18 - *Preparation of 3-(3¹,3¹-diethylureido)-2-dimethylamino-1,4-naphthoquinone*

This compound was prepared using a method analogous to that of Example 17. Yield 25%, 96-97°C.

Analysis Calculated for $N_3O_3C_{17}H_{21}$ C 64.7; H 6.7; N 13.3
Found C 65.2; H 6.5; N 13.0

Example 19 - *Preparation of 2-methylamino-3-(3-methylureido) -1,4-naphthoquinone*

Methylisocyanate (2 ml) was added dropwise to a stirred solution of the compound prepared in Example 30 hereinafter (2g) in benzene (50 ml). After refluxing the mixture for 0.5 hours the solution was cooled and precipitate filtered off to give the desired compound (42%) m.p., 238-239°C (ethanol).

Analysis Calculated for $N_3O_3C_{13}H_{13}$ C 60.2; H 5.1; N 16.2
Found C 59.9; H 5.1; N 16.0

Examples 20 and 21

The following two compounds were prepared by methods analogous to that of Example 19:–

2-(3-Isopropylureido)-3-methylamino- 1,4-naphthoquinone; m.p. 213-215°C; Yield 47% (Example 20)

2-Methylamino-3(3,3-dimethylureido) -1,4-naphthoquinone, m.p. 238-239°C; Yield 35% (Example 21)

Example 22 - *Preparation of 3-chloro-2-ureido- 1,4-naphthoquinone*

2-Amino-3-chloro-1,4-naphthoquinone (20g) was heated in excess chlorosulphonylisocyanate for 1 hour with stirring at 60°C. After cooling, the mixture was poured dropwise (with great caution) onto ice and left to stand overnight. The yellow solid was filtered off and crystallised out from the mother liquor residues to give the desired product (0.3g), m.p. dec>198°C (ethanol).

Analysis Calculated for $N_2O_3C1C_{11}H_7$ C 52.8; H 2.75; N
Found C 52.9; H 2.7; N 10.8

Example 23 - *Preparation of 2-bromo-3-(3- methylureido)- 1,4-naphthoquinone*

Bromine (0.5g) in acetic acid was added to a stirred solution of 3-methylureido-1,4-naphthoquinone in acetic acid at 20°C. After 30 minutes stirring the mixture was poured into water and extracted with CH_2Cl_2. Evaporation of the dried solution yielded a solid residue which on addition of ethanol left an insoluble yellow solid. After

drying the solid 2-bromo-3-(3-methylureido)- 1,4-naphthoquinone (0.1g) was obtained. m.p. 194-195°C (decomposition).

Analysis Calculated for $N_2O_3C_{12}H_9$ C 46.6; H 2.9; N 9.0
Found C 46.9; H 2.9; N 8.7

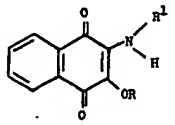
Example 24 - Preparation of 3-ethoxy-2-methylamino- 1,4-naphthaquinone

Dry HCl was passed into an ethanolic solution of 2-dimethylamino-3-nitrosomethylamino- 1,4-napthoquinone (2g) for 10 minutes or until denitrosation was completed (TLC). The dark solution was poured into water and extracted with methylene chloride. After evaporation of CH_2Cl_2 the residue was chromatographed on silica gel in CH_2Cl_2. The first coloured fractions obtained were evaporated to give 3-ethoxy-2-methylamino-1,4-naphthoquinone (?.9g) m.p. 91-92°C.

Analysis Calculated for $C_{13}H_{13}NO_3$ C 67.5; H 5.7; N 6.06
Found C 67.4; H 5.6; N 5.9

Examples 25 - 28

The following compounds were prepared by a method analogous to that described in Example 24.



Example	R^1	R	m.p. (°C)
25	CH_3	$CH(CH_3)_2$	91-92
26	CH_3	CH_3	158-159
27	C_2H_5	$CH(CH_3)_2$	69-70
38	$CH(CH_3)_2$	$CH(CH_3)_2$	oil

Example 29 - Preparation of 2-methylamino-3- isopropylamino- 1,4-naphthoquinone

2-(N-methyl-N-nitrososmino)-3-isopropylamino- 1,4-naphthoquinone (1.4g) was added portionwise to a saturated solution of HCl in methanol (50 ml). The mixture was refluxed for 10 minutes, cooled and evaporated to dryness. The residue was added to water (100 ml) containing triethylamine. The precipitated purple solid was filtered off, dissolved in ethanol and reprecipitated with water to give after air drying 2-methylamino-3-isopropylamine-1,4-napthoquinone (0.7 g), m.p. 72-73°C.

Analysis Calculated for $N_2O_2C_{14}H_6$ C 68.8; H 6.6; N 11.5
Found C 69.3; H 6.4; N 11.2

Example 30 - Preparation of 3-amino-2-methylamino- 1,4-naphthoquinone

This compound was prepared by a method analogous to that used in Example 29. Yield 51%, m.p. 135-138°C.

Analysis Calculated for $N_2O_2C_{14}H_{16}$ C 68.8; H 6.6; N 11.5
Found C 69.3; H 6.4; N 11.2

Example 31 - Preparation of 2,3-diamino-1,4-naphthoquinone

A suspension of 2,3-dichloro-1,4-naphthoquinone (22.7g; 0.1 M) in acetonitrile (250 ml) was refluxed with potassium phthalimide (37.0g; 0.2 M) for 5 hours. The cooled mixture was filtered and the solid washed with ethanol/water (1:1) and ether, to give crude 2,3-bis-phthalimido-1,4-naphthoquinone (30g). This crude product (22.7) was stirred for 1 hour in an aqueous solution of hydraxine hydrate (35 ml 80%). The brown precipitate was filtered off and stirred for one hour with hydrazine hydrate (30 ml) at 70-75°C. The cooled mixture was filtered and the solid washed with water and dried in vacuo to give 2,3-diamino-1,4-naphthoquinone (9g), m.p. 220°C (benzene).

Analysis Calculated for $NO_2SC_{10}H_7$ C 58.5; H 3.4; N 6.8
Found C 58.9; H 3.2; N 6.8

Example 32 - *Preparation of methyl N-(3-diethylamino-7-methyl- 1,4-dioxanaphth-2-yl)carbamate*

Methyl N-(3-chloro-7-methyl-1,4-dioxonaphth-2-yl)carbamate (2g) in methylene chloride was reacted with excess diethylamine. The mixture was stirred at room temperature for 3 hours and then washed with water. After evaporation of CH_2C1_2 the residue was chromatographed on silica gel using CH_2C1_2 as eluant. The first fractions obtained were evaporated to give the desired product. m.p. 108-110°C.

Analysis Calculated for $C_{17}H_{20}N_2O_4$ C 64.5; H 6.4; N 8.8
Found C 64.5; H 6.3; N 8.7

Example 33

The herbicidal activity of some of the compounds synthesised in the preceding examples is demonstrated by the following tests.

To evaluate their herbicidal activity, the compounds of the invention were tested using as a representative range of plants:– maize, *Zea mays* (Mz); rice, *Oryza sativa* (R); barnyard grass, *Echinchloa crusgalli* (BG); pea, *Pisum* sativum (P); linseed, *Linum usitatissium* (L); mustard, *Sinapis alba* (M); and sugar beet, *Beta vulgaris* (SB. In one example oats, *Avena sativa* and rye grass *Loluim perenne* were used in place of rice and barnyard grass respectively.

The tests fall into two categories, pre-emergence and post-emergence. The pre-emergence tests involved spraying a liquid formulation of the compound onto the soil in which the seeds of the plant species mentioned above had recently been sown. The post-emergence test involved two types of test, viz. soil drench and foliar spray tests. In the soil drench tests the soil in which seedling plants of the above species were growing, was drenched with a liquid formulation containing a compound of the invention and in the foliar spray tests the seedling plants were sprayed with such a formulation.

The soil used in these tests was a steam-sterilised, modified John Innes Compost mixture in which half the peat, by loose bulk, had been replaced by vermiculite.

The formulations used in the tests were prepared by diluting with water solutions of the compounds, in acetone containing 0.4% by weight of an alkylphenol/ethylene oxide concentrate available under the trade name Triton X-155 (Trade Mark). In the soil spray and foliar spray tests the acetone solutions were diluted with an equal volume of water and the resulting formulations applied at two dosage levels corresponding to 10 and 1 kilograms of active material per hectare respectively in a volume equivalent to 400 litres per hectare. In the soil drench tests one volume of the acetone solutions was diluted to 155 volumes with water and the resulting formulation applied at one dosage level equivalent to 10 kilograms of active material per hectare in a volume equivalent to approximately 3,000 litres per hectare.

In the pre-emergence tests untreated sown soil and in the post-emergence tests untreated soil bearing seedling plants were used as controls.

The herbicidal effects of the compounds were assessed visually seven days after spraying the foliage and drenching the soil and eleven days after spraying the soil, and were recorded on a 0-9 scale. A rating 0 indicates no effect on the treated plants, a rating 2 indicates a reduction in fresh weight of stem and leaf of the plants of approximately 25%, a rating 5 indicates a reduction of approximately 55%, a rating 9 indicates a reduction of 95% etc.

The results of the tests are set out in the Table.

TABLE

Example No.	Post-Emergence															Pre-Emergence						
	Dosage kg/ha	Soil Drench							Dosage kg/ha							Soil Spray						
		MZ	R	BG	P	L	M	SB		MZ	R	BG	P	L	M	SB	MZ	R	BG	P	L	M	SB
1	10	3	2	7	2	1	9	0	10	21	20	95	101	99	13	51	50	00	91	00	79	92	70
3	10	0	0	0	0	0	0	0	10	41	20	74	203	99	31	90	0	0	0	0	0	0	0
7	10	0	0	0	0	0	0	0	10	20	71	75	512	99	26	71	0	0	0	0	0	0	0
8	10	0	0	0	0	0	0	0	10	21	31	85	005	99	99	61	0	0	0	0	0	0	0
11	10	9	1	3	2	1	9	0	10	99	83	97	977	99	79	99	98	72	82	03	99	37	93

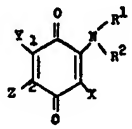
TABLE (continued)

Example No.	Post-Emergence: Dosage kg/ha	Post-Emergence: Soil Drench MZ	R	BG	P	L	M	SB	Post-Emergence: Dosage kg/HA	Post-Emergence MZ	R	BG	P	L	M	SB	Pre-Emergence: Soil Spray MZ	R	BG	P	L	M	SB
16	10	5	7	5	0	2	7	5	10	5	4	9	6	8	9	7	8	9	7	3	5	8	8
									1	2	2	8	5	8	9	7	0	5	0	0	0	2	0
19	10	0	0	3	5	0	0	0	10	3	0	7	2	3	3	5	0	9	9	2	4	9	8
									1	0	0	2	0	0	1	0	0	3	0	0	0	4	2
21	10	0	0	3	1	0	0	0	1	5	1	9	3	5	8	1	0	2	2	0	0	2	1
25	10	1	0	7	1	5	1	0	10	2	8	9	2	9	9	9	1	4	9	8	8	9	7
									1	1	1	3	1	9	9	6	0	1	1	0	0	0	0
31	20	0	1	7	5	9	2	2	10	1	0	7	2	9	9	5	0	0	0	0	2	2	0
										0		3	0	7	7	3					0	0	
32	10		0	0	0	0	0	0	5	8	4	9	3	9	9	9	0	0	5	0	3	5	0
									1	2	2	8	1	9	9	5			0		0	2	

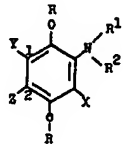
* Oats and rye-grass used in place of rice and barnyard grass respectively

WHAT WE CLAIM IS:-

1. A herbicidal composition comprising a carrier together with as active ingredient a compound having one of the following general formulae:-



(I)



(II)

wherein

R^1 is hydrogen, alkyl, alkoxy, alkylcarbonyl, cycloalkyl, aryl, or an -NO or $-CONR^3R^4$ group;

X is halogen, alkoxy, or an $-NR^3R^4$ or -NHCOO-alkyl group;

R^3 and R^4 each individually represent hydrogen, alkyl, aminoalkyl, or alkylaminoalkyl;

Y and Z together with carbon atoms 1 and 2 represent a benzene, thiophen, thiadiazole or thiazole ring each of which rings may be substituted by an alkyl group; and

R is alkyl, alkylcarbonyl, arylcarbonyl, the alkyl or aryl groups of which may be optionally substituted by halogen,

or where the compound is capable of forming a quaternary ammonium salt, the quaternary ammonium salt thereof; provided that

(a) for the groups alkoxy, alkylcarbonyl, NO and $-CONR^3R^4$, R^1 is not the same as R^2;

(b) in formula (I) R^1 or R^2 can only be an alkylcarbonyl group when Y and Z together with carbon atoms 1 and 2 form a thiophen, thiazole or thiadiazole ring;

(c) when R^1 is hydrogen and R^2 is alkylcarbonyl X does not represent an -NH-alkyl group; and

(d) when R^1 is hydrogen and R^2 is alkyl, X does not represent an -NHCOO-alkyl group.

2. A herbicidal composition according to claim 1 in which the active ingredient has the general formula I or II wherein

R^1 is hydrogen, alkyl of 1 to 4 carbon atoms, alkoxy of 1 to 4 carbon atoms, alkylcarbonyl of 2 to 5 carbon atoms, cycloalkyl of up to 6 carbon atoms, or an -NO or-$CONR^3R^4$ group;

R^2 is hydrogen, alkyl of 1 to 4 carbon atoms, alkoxy of 1 to 4 carbon atoms, alkylcarbonyl of 2 to 5 carbon atoms, -NO, or a $-CONR^3R^4$ group;

X is chlorine, bromine, alkoxy of 1 to 4 carbon atoms, $-NR^3R^4$, or an -NHCOO-alkyl group of up to 5 carbon atoms;

R^3 and R^4 each individually represent hydrogen, alkyl of 1 to 4 carbon atoms, aminoalkyl of 1 to 4 carbon atoms, or alkylaminoalkyl of up to 8 carbon atoms;

Y and Z together with carbon atoms 1 and 2 represent a benzene, an alkyl benzene, or a thiophen ring;

R is alkyl of 1 to 4 carbon atoms, alkylcarbonyl of 2 to 5 carbon atoms, arylcarbonyl of up to 15 carbon atoms or haloalkyl of 1 to 4 carbon atoms;

and where the compound is capable of forming a quaternary ammonium salt, the quaternary ammonium salt thereof with an alkyl halide of 1 to 4 carbon atoms or with an alkyl sulphate.

3. A herbicidal composition according to claim 1 wherein the active ingredient has the general formula I or II wherein

R^1 is hydrogen, methyl, ethyl, isopropyl or cyclopropyl;

R^2 is hydrogen, methyl, ethyl, propyl, isopropyl, methylcarbonyl, ethylcarbonyl, -NO, aminocarbonyl, methylaminocarbonyl, dimethylaminocarbonyl, diethylaminocarbonyl or isopropylaminocarbonyl;

X is chlorine, bromine, methoxy, ethoxy, isopropoxy, amino, methylamino, dimethylamino, isopropylamino, dimethylaminoethylamino, dimethylaminopropylamino, or methoxycarbonylamino;

Y and Z together with carbon atoms 1 and 2 represent a benzene, an alkylbenzene or a thiophen ring;

R is acetyl or chloroacetyl;

and where the compound is capable of forming a quaternary ammonium salt, the quaternary salt thereof with methyl iodide, chloride or bromide, or with dimethyl sulphate.

4. A herbicidal composition according to claim 1, wherein the compound of general formula I or II is any one of those mentioned in Examples 1 to 33 herein.

5. A herbicidal composition according to any one of claims 1 to 4 which comprises at least

two carriers, at least one of which is a surface-active agent.

6. A method of combating undesired plant growth at a locus which comprises applying to the locus a compound of the general formula I or II defined in claim 1 or a quaternary ammonium salt thereof or a herbicidal composition as claimed in any one of claims 1 to 5.

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